

“Contributions to the Chemistry of Chlorophyll. No. II.” By
EDWARD SCHUNCK, F.R.S. Received November 25,—Read
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[PLATE 1.]

Considering the intimate though as yet little understood connexion between chlorophyll and the carbon dioxide of the atmosphere, it seemed to me that it might be of interest to ascertain whether compounds of phyllocyanin, similar to those previously described, could be obtained, in which the organic or other acid should be replaced by carbonic acid.

On passing a current of carbon dioxide through a solution of phyllocyanin in absolute alcohol holding a quantity of freshly precipitated hydrated ferrous oxide in suspension, no combination took place, the phyllocyanin remaining unchanged, though the current of gas was passed through the liquid for a considerable time.

On substituting freshly precipitated cupric oxide for the ferrous oxide there were slight indications of some reaction taking place, but the phyllocyanin remained for the most part uncombined.

A much more decided effect is produced when zinc oxide is employed. On passing a current of carbon dioxide for several hours through an alcoholic solution of phyllocyanin holding hydrated zinc oxide in suspension, the colour of the liquid changes by degrees, the dull phyllocyanin tint disappearing. On being filtered from the excess of zinc oxide (which retains a pale-green tint, not removable by washing with alcohol) it appears of a fine bluish-green; it fluoresces strongly, and shows absorption-bands which coincide with those of the alcoholic solution of phyllocyanin zinc acetate. The liquid leaves on evaporation a dark-green semi-crystalline residue, which may be heated to 150° without undergoing any change, but is decomposed at a temperature of 160 — 170° . It is, however, very easily decomposed by the action of strong acids. On adding a little hydrochloric acid to its alcoholic solution and heating, bubbles of gas are seen to escape, the colour of the solution changes to blue, and on now adding water there is a dull flocculent precipitate, which dissolves easily on shaking up with ether, the solution showing the colour and absorption-bands peculiar to phyllocyanin solutions. There can be no doubt, therefore, that the compound formed is a phyllocyanin zinc carbonate, which by the action of strong acids is decomposed, yielding phyllocyanin and carbon dioxide. An alcoholic solution of the compound exposed in an open test-tube to sunlight soon loses its bright-green colour and becomes yellow, the absorption-bands at the same time disappearing.

The compounds of phyllocyanin containing zinc are in some respects not unlike chlorophyll itself, or rather the green constituent of chlorophyll, and it was, therefore, natural to suppose that the peculiar effects observed when zinc powder was made to act on Hoppe-Seyler's chlorophyllan (impure phyllocyanin?) were due to regenerated chlorophyll. The phyllocyanin zinc compounds, like chlorophyll itself, yield bright green strongly fluorescent solutions; they are easily decomposed by strong acids, and they are rapidly changed under the combined influence of air and light. The absorption spectrum of the phyllocyanin zinc compounds consists like that of chlorophyll of four bands, but the bands do not exactly coincide with those of chlorophyll as regards position and relative intensity. In making such comparisons it must not of course be forgotten that what we in a general way call chlorophyll is a mixture, the components of which have not hitherto been separated from one another in a satisfactory manner.

The various double compounds of phyllocyanin are not equally susceptible to the influence of air and light; they differ as much in this respect, *inter se*, as do phyllocyanin and chlorophyll, the former being a very stable body, the latter exceedingly unstable. The compounds containing zinc are most easily changed, while those containing copper are very permanent. These differences were clearly manifested in an experiment of which the results were as follows:—A dilute alcoholic solution of phyllocyanin was divided into four equal parts. In one part the phyllocyanin was left uncombined; in the second part it was by the addition of acetic acid and zinc oxide and boiling changed into phyllocyanin zinc acetate, while in the third and fourth parts it was in like manner converted into phyllocyanin ferrous acetate and phyllocyanin cupric acetate respectively. All four liquids having been made equal in volume by the addition of alcohol where required, were exposed from the end of July in loosely stoppered cylinders to alternate sunlight and diffused daylight, an alcoholic solution of chlorophyll of approximately the same intensity as the phyllocyanin zinc acetate solution being placed in a fifth vessel at the side. After three days' exposure the chlorophyll solution had become nearly colourless, though it still showed bands due to reformed phyllocyanin. After one week's exposure the phyllocyanin zinc acetate solution had in like manner lost the greater part of its green colour, retaining only a faint greenish-yellow tinge with a slight fluorescence, and showing a faint band in the red. After a fortnight's exposure the solution appeared nearly colourless, and the band in the red could only be seen when the light passed through a considerable thickness of liquid, while the other solutions were quite unaltered as regards colour and absorption-bands. After a further exposure of five weeks the phyllocyanin solution had become much

paler, though still showing the characteristic absorption-bands, while in the solution of the ferrous compound only a faint indication of the band in the red could be seen, the solution of the cupric compound remaining quite unchanged as regards intensity of colour and distinctness of absorption. After a still further exposure the absorption-bands of the phyllocyanin solution had nearly disappeared, only a faint indication of the one in the red remaining, but no change could be perceived in the solution of the cupric compound. It appears, therefore, that while the zinc compound shows far less stability when exposed in solution to the action of air and light than uncombined phyllocyanin, being indeed almost as unstable as chlorophyll itself, the cupric compound is far more stable, the ferrous compound occupying in this respect a position intermediate between that of the zinc compound and that of uncombined phyllocyanin. There are few compounds of colouring matters which would withstand the combined action of light and oxygen for so long a period as phyllocyanin cupric acetate. The instability of the zinc compound must be due to the nature of the compound itself, for it is difficult to suppose that the metallic base can in any way assist in the process of oxidation, for such the process must be.

Action of Caustic Alkali and Zinc on Phyllocyanin.—When phyllocyanin is treated with boiling caustic potash lye to which zinc powder is added, it dissolves rapidly, yielding a dark greenish-blue solution, which after filtration from the excess of zinc, gives with acetic acid a green precipitate. This precipitate, after filtration and washing, dissolves in ether, giving a fine bluish-green fluorescent solution, which resembles the solutions of phyllocyanin zinc acetate, but shows a slightly different spectrum, all the bands except the first being further away from the red. The ethereal solution leaves on spontaneous evaporation an amorphous residue, which is green by transmitted, purple by reflected light. When instead of acetic acid hydrochloric acid is added to the greenish-blue alkaline solution, there is a dark green precipitate, which differs from phyllocyanin inasmuch as its ethereal solution is greener and far more fluorescent than an ethereal solution of the latter, and shows a spectrum of five bands, all of which lie further away from the red than the corresponding ones of phyllocyanin. It is probable that the precipitate with hydrochloric acid consists of a product formed by the reducing action of zinc on phyllocyanin, whereas the precipitate with acetic acid represents the double compound of this body with zinc and acetic acid, being formed when acetic acid is added to the solution containing the product of reduction along with zinc oxide.

Action of Hydrochloric Acid and Metallic Tin on Phyllocyanin.—When metallic tin is added to a solution of phyllocyanin in concentrated hydrochloric acid, the solution on standing gradually loses its

bright bluish-green colour, which changes to a dull olive-green. The addition of water to the solution produces a brown precipitate, which being filtered off and washed to remove the acid, dissolves much more easily in boiling alcohol than phyllocyanin, giving a dark olive-coloured solution. This solution leaves on evaporation a brown amorphous residue, which treated with ether dissolves for the most part. The ethereal solution has a green colour with a tinge of red, and shows a spectrum consisting of eight bands; it leaves on evaporation a semi-crystalline residue, which is green by transmitted, purple by reflected light. On the addition of concentrated hydrochloric acid it separates into two distinct layers, the upper one being colourless, while the lower one is green, and shows four bands.

By the prolonged action of tin on the solution of phyllocyanin in hydrochloric acid, a further and more complete change is effected, the solution acquiring a bright red colour without the least tinge of green. On adding water the solution gives a red flocculent precipitate, which filtered off and washed appears dark red, the filtrate retaining an orange colour, and showing a broad ill-defined band, covering part of the green and blue. The precipitate dissolves almost entirely in warm alcohol, giving a bright red solution. This solution, on adding a little caustic alkali, acquires a bright lemon-yellow colour, but the red colour is restored by an excess of hydrochloric acid; the alkaline solution shows a broad band between the green and blue, but on standing a short time exposed to the air it changes, becoming of a deeper yellow, and it now shows a spectrum of three bands, one in the yellow, one in the green, both pale, with a dark band between the green and blue. The red alcoholic solution leaves on spontaneous evaporation a reddish-brown amorphous residue, which dissolves only in part in boiling ether, giving a reddish-brown solution, which shows a peculiar spectrum of six bands. The body showing this spectrum is probably a product of oxidation of the red substance. The acid liquid filtered from the red precipitate, after removing the tin with sulphuretted hydrogen, is found to contain a mere trace of organic matter.

The colouring matter formed by the action of tin and hydrochloric acid on phyllocyanin resembles in some respects those contained in the petals of red flowers. Hitherto, however, I have not succeeded in finding among the latter any one exactly like it.

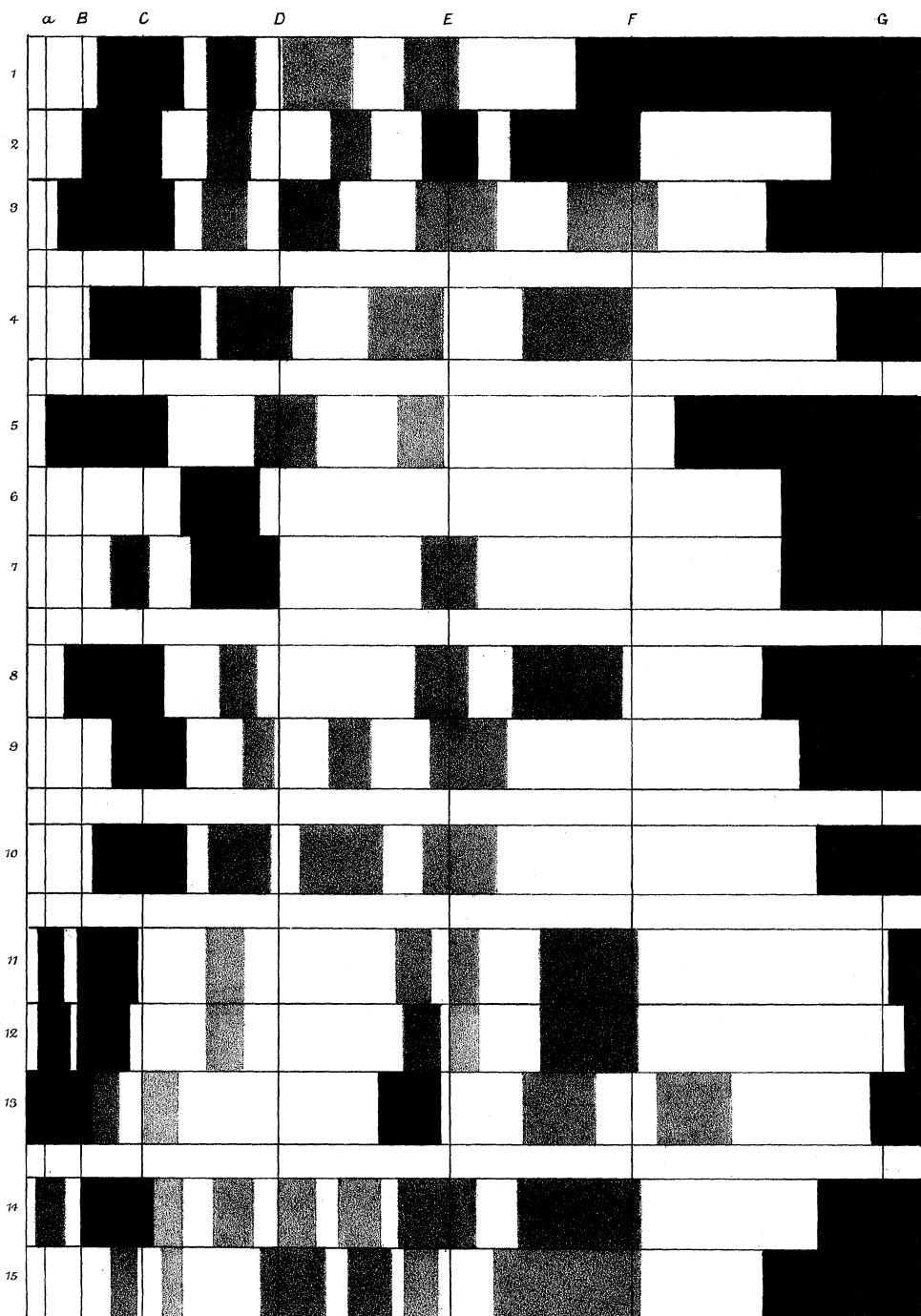
Examination of the Mother-liquors of Phyllocyanin.—Having some reason to suspect that the acetic acid mother-liquors of phyllocyanin contained some other substance similar to it of definite character, I added water to a portion of these liquors, so as to throw down the whole of the colouring matter contained in it. The flocculent precipitate was filtered off and dissolved in boiling alcohol. The solution on cooling gave a crystalline deposit which was found to possess

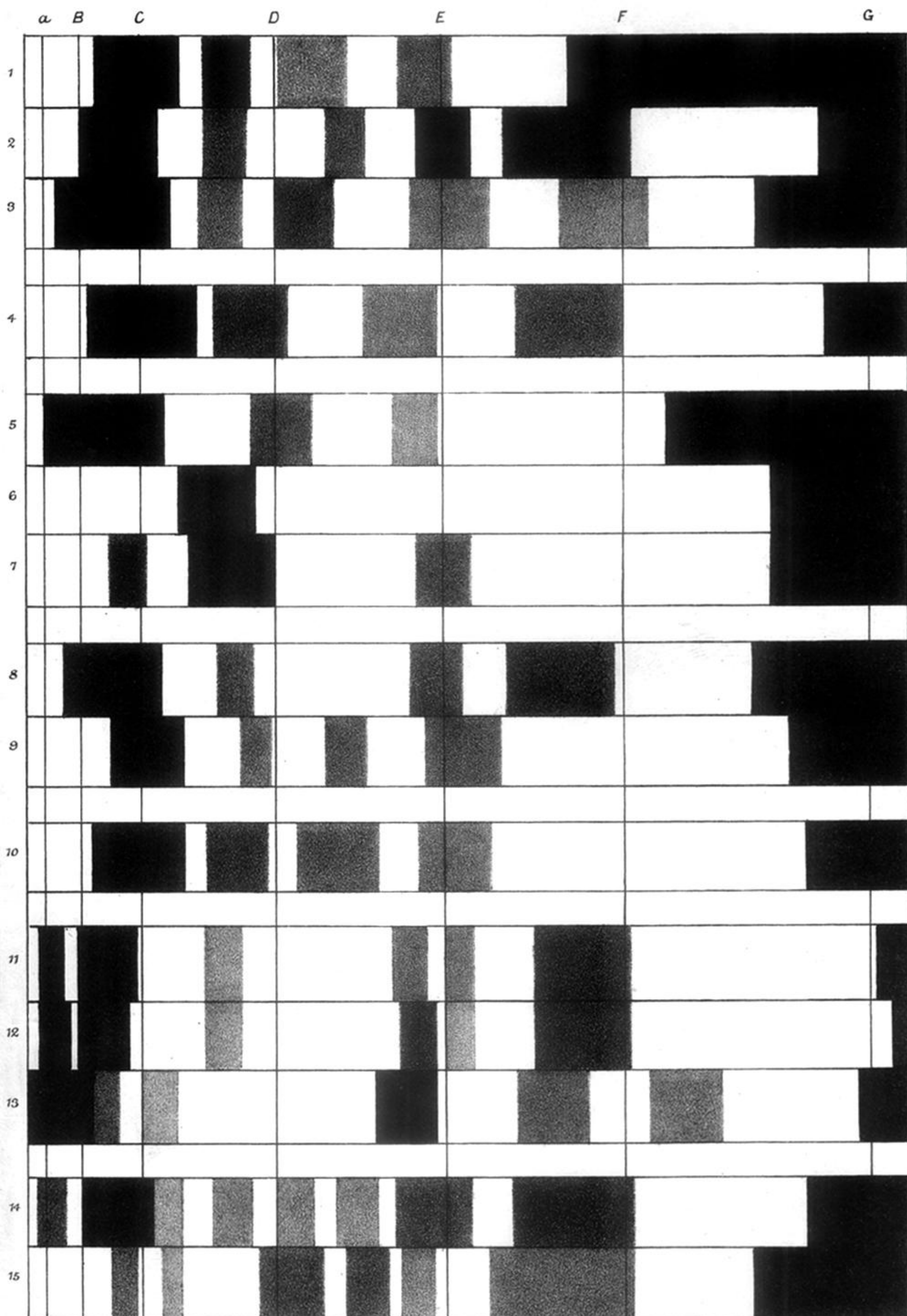
all the properties of phyllocyanin. I think therefore that the mother-liquors contained that colouring matter only, along with fatty matters and other impurities.

EXPLANATION OF PLATE.

Absorption Spectra of Phyllocyanin and its principal Compounds and Derivatives.

1. Chlorophyll in alcohol. This spectrum is given merely for the sake of comparison, not as a new representation of what has so frequently been depicted by others.
2. Phyllocyanin in ether.
3. Phyllocyanin in concentrated hydrochloric acid.
4. Phyllocyanin cupric acetate in ether.
5. Phyllocyanin ferrous palmitate in alcohol.
6. Phyllocyanin ferrous palmitate after treatment with hydrochloric acid in the cold.
7. Phyllocyanin ferrous palmitate after treatment with boiling hydrochloric acid.
8. Phyllocyanin ferrous malate in alcohol.
9. Phyllocyanin ferrous malate after treatment with hydrochloric acid.
10. Phyllocyanin zinc carbonate in alcohol. This spectrum should be compared with that of chlorophyll.
11. Product obtained by treating phyllocyanin with caustic alkali, then with acetic acid, in ether.
12. Product formed by the further action of acetic acid on the preceding, in ether.
13. Product of the action of alcoholic potash or soda on phyllocyanin, in ether.
14. First product of the action of tin and hydrochloric acid on phyllocyanin, in ether.
15. Final product of the action of tin and hydrochloric acid on phyllocyanin, in ether.





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